APPENDIX 4A
ANALYTICAL RESULTS OF CHEMICAL AGENTS

APPENDIX 4A
INTRODUCTION

This appendix presents summaries of data obtained from a series of analyses of chemical agents and their neutralents and the calculated compositions derived from those results. The results for the chemical agents HD, GB, and VX represent munitions grade material. Munitions grade agent represents the quality of agent that has been loaded into munitions upon manufacture. Some agent degradation or contamination may have occurred between the time of munition manufacture and its recovery from a storage or burial site. The data used to calculate the composition of the treated agents were obtained from several types of chemical analyses of laboratory-produced neutralents and process knowledge, as discussed below.

In 1995 and 1996, a random sampling of the HD stored in ton containers at Aberdeen Proving Ground (APG), Maryland, and a random sampling of VX, also in ton containers, at Newport, Indiana, was performed to assess the composition of these stockpiled agents. In addition, HD, GB, and VX samples were removed from stored stock at APG for analysis and treatment studies at Edgewood Research, Development and Engineering Center (ERDEC). The results of these analyses are presented in tables, as follows:

- Chemical Agent GB - The data in this table are for one sample of munitions grade GB [ERDEC, Evaluation of the Chemistry which Supports the Munitions Management Device - 1 (MMD-1) for Chemical Agent GB Neutralization Process in Both MEA/H_2O and KOH/CH_3OH/H_2O, for Program Manager, Non-Stockpile Project, Draft Report, 28 August 1996].

- Chemical Agent HD - This table summarizes data from the analysis of 27 HD samples from ton containers at APG (W.F. Willoughby, et al., EAI Corp. for ERDEC, Bulk Agent Stockpile Survey, Final Report, No. EAI 52/95/006F, April 1996), plus three samples used by ERDEC in studies of the treatment of HD [see ERDEC, Evaluation of the Chemistry which Supports the Munitions Management Device - 1 (MMD-1) for Chemical Agent HD Neutralization Process, for Program Manager, Non-Stockpile Project, Draft Report, 14 August 1996].

- Chemical Agent VX - This table summarizes data from the analysis of 32 VX samples from ton containers at the Newport Chemical Activity, Newport, Indiana (W.F. Willoughby, et al, EAI Corp. for ERDEC, Bulk Agent Stockpile Survey, Final Report, No. EAI 52/95/006F, April 1997), plus two samples used byERDEC in studies of the hydrolysis of VX [see PMCD, AVX Nerve Agent Laboratory Test Report@ (Final), Alternative Technology Program, 5 November 1996].

The treatment residues, or neutralents, from HD, GB, and VX were obtained from laboratory tests that used the same neutralization reagent that will be used in the MMD-1. The three tables at the end of this appendix summarize the calculated compositions that are based on the results of several analyses on a series of neutralents in each case. For the HD and GB neutralents, tests of the flashpoint, the pH, and stability were performed to establish the Resource, Conservation, and Recovery Act ignitability, corrosivity, and reactivity characteristics. For VX, these characteristics were estimated based on a knowledge of the neutralization. The characteristics are also included in each agent table. These analyses are reported in three draft reports from ERDEC with the common title:

Evaluation of the Chemistry which Supports the Munitions Management Device - 1 (MMD-1) for Chemical Agent *HD, GB, or VX* Neutralization Process in *reagent solution* , for Program Manager, Non-Stockpile Project, Draft Report.

For each chemical agent (HD, GB, or VX), the reagent solutions varied as listed below:

- HD Report: Reagent solution - monoethanolamine (MEA)/water (not in title of report)
- GB Report: Reagent solution - ABoth MEA/H_2O and KOH/CH_3OH/H_2O,@ dated 28 August 1996
- VX Report: Reagent solution - ABoth $KOCH_2CH_2NH_2$/MEA and NaOH/H_2O/MEA,@ dated 26 October 1996.

Chemical Agent GBComposition

Based on Analysis of One Sample from Ton Container Storage[a]

Major Components (Concentration: > 0.55%)	Result
GB: isopropyl methylphonofluoridate	88.0%
DIMP: diisopropyl methylphosphonate	7.84%
TBA: tributylamine	2.18%
ethyl isopropyl methylphosphonate	0.53%
ethyl methylphosphonofluoridate	0.52%
N,N=-diisopropylurea	0.52%
Minor Components (Concentration < 0.55%)	
N,N=-diisopropylthiourea	0.22%
DICDI: diisopropylcarbodiimide	570 ppm
unknown (molecular wt.: 214)	570 ppm
O-isopropyl dimethylphosphinate	320 ppm
methylphosphonic difluoride	230 ppm
dibutylisopropylamine	150 ppm
diisopropylbutylamine	140 ppm

NOTE:
a Assay of GB equaled 88.0 weight percent by NMR. Other component weight ratios were calculated from their molecular weights and the area percent values by GC/MSD/EI procedure. Concentrations were normalized to a total of 12 percent other impurities

Chemical Agent HD
Composition Based on Analyses of 30 Samples from Ton Container Storage

Major Components (Average conc. > 1.2%):	Occurrence[a]	Range
HD: 2-chloroethyl sulfide	30	83.6-95.0%
Q: 1,2-bis(2-chloroethylthio)ethane	30	0.06-6.0%
1,4-dithiane	30	0.47-3.64%
2-chloroethyl 4-chlorobutyl sulfide	30	0.28-1.73%
2-chloroethyl 3-chloropropyl sulfide	24	0-2.49%
Iron, calculated as ferrous chloride	27	0.008-1.38%
HD disulfide: bis(2-chloroethyl) disulfide	20	0-4.31%
Other $C_6H_{12}Cl_2S$ isomers	24	0-0.92%
Minor Components (0.1 to 0.5%):		
2-chloropropyl sulfide	27	0-1.03%
1,2-dichloroethane (D028)*	30	0.058-0.78%
3-chloropropyl sulfide	3	0-0.37%
2-chloropropyl 3-chloropropyl sulfide	3	0-0.37%
hexachloroethane (D034)*	2	0-2.99%
tetrachloroethylene (D039)*	10	0-1.51%
Trace Components (< 1000 ppm):		
1,2,5-trithiepane	10	0-5,000 ppm
chlorobenzene (D021)*	1	0-1,600 ppm
1,4-thioxane	27	0-2,700 ppm
HD trisulfide: 2-chloroethyl trisulfide	10	0-6300 ppm
2-chloroethyl (2-chloroethoxy)ethyl sulfide	3	0-11,000 ppm
2-(2-chloroethylthio)ethyl vinyl sulfide	1	0-810 ppm
2-chlorobutyl 2-chloroethyl sulfide	1	0-810 ppm
1,1,2,2-tetrachloroethane	4	0-8300 ppm
11-chloro-6-oxa-3,9-thiaundecene	1	0-570 ppm
HD sulfoxide: 2-chloroethyl sulfoxide	1	0-490 ppm
2-(2-chloroethylthio)ethyl vinyl ether	1	0-490 ppm
Trace Components (< 1000 ppm) (Continued):		
2-methyl-1-propene or isobutylene	23	0-600 ppm
thiirane	22	0-600 ppm
10-chloro-2-oxa-5,8-thiadecane	1	0-325 ppm
2-chloroethyl ethyl sulfide	1	0-160 ppm
copper (as cupric chloride)	14	0-100 ppm
2-chlorobutane	3	0-300 ppm
trichloroethylene (D040)*	1	0-200 ppm

NOTES:

a Number of samples in which the component was found.

* Substance regulated under RCRA toxicity characteristic regulation; waste number is shown in parentheses.

Chemical Agent VX
Composition Based on Analyses of 34 Samples from Ton Container Storage

Major Components (Average conc. >0.5%):	Occurrence[a]	Range
VX: O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate	34	87.1-95.6%
DCCDI: dicyclohexylcarbodiimide	2[b]	0-3.59%
DICDI: diisopropylcarbodiimide	32	0-3.82%
P,P=-diethyl dimethyldiphosphonate	34	0.19-2.7%
2-diisopropylaminoethanethiol	34	0.25-2.23%
BIS-VX: bis-S,S-(2-diisopropylaminoethyl) methylphosphonate	2[c]	0-1.42%
1,2-bis-(ethyl methylphosphonothiolo)ethane	32	0-1.45%
Minor Components (Average conc. >0.5 and <0.1%):		
QB: O-(2-diisopropylaminoethyl) O=-ethyl methylphosphonate	29	0-0.96%
P,P=-diethyl dimethyldiphosphonomonothioate	25	0-1.06%
O-ethyl methylethylphosphinate	7	0-0.42%
O,O=-diethyl methylphosphonothioate	24	0-0.40%
diisopropylamine	34	0.04-0.33%
2-(diisopropylamino)ethyl ethyl sulfide	27	0-1.21%
S-[2-(ethylisopropylamino)ethyl] O-ethyl methylphosphonothioate	1	0-0.15%
O,S-diethyl methylphosphonothioate	32	0-0.47%
DEMP: diethyl methylphosphonate	34	0.03-0.8%
S-(diisopropylaminoethyl) O-ethyl methylphosphonodithioate	1	0-0.07%
Trace Components (< 0.1%):		
1,3-diisopropylurea	6	0-910 ppm
N,N-diisopropylethylamine	10	0-280 ppm
N,N-diisopropylmethylamine	10	0-240 ppm
acetone	30	20-320 ppm
Trace Components (< 0.1%) (Continued):		
1,3-dicyclohexylurea	2	0-100+ ppm
unknowns (13 substances have been detected)	0-26[d]	0.1-1%[d]

NOTES:

a The number of samples in which the component was found by analysis. Assays of VX by weight percent were determined by the GC/TCD method. The other component weight ratios were calculated from their molecular weights and the area percent values by a GC/MSD/EI procedure and the concentrations were normalized to weight percent of the difference of the VX concentration and 100 percent.

b The older lots of munition grade VX used dicyclohexylcarbodiimide (DCCDI) rather than the diisopropylcarbodiimide (DICDI) as a stabilizer. The corresponding urea (1,3-dicyclohexyl- or 1,3-diisopropyl-) is formed from the stabilizer.

c The BIS-VX was determined by the ^{31}P NMR method of analysis in one sample to produce the 1.42% value. In four other munitions grade material, BIS-VX was found at 0.4 to 0.8 percent by the ^{31}P NMR method.

d These unknown components of varying types, and various amounts have been found in most of the munitions grade VX. The maximum level in the range is estimated.

ATTACHMENT 4, APPENDIX A-1
WASTE ANALYSIS RESULTS OF TREATED CHEMICAL AGENTS
HD, GB, AND VX
HD Neutralent Composition[a,b]

Major Components (Concentration: > 0.1%):	Calculated or	Notes[c]:
MEA: monoethanolamine	67-89%	P; NR
water	8.9-9.9%	P; NR
MEA·HCl: 2-hydroxyethylammonium chloride or	0.9-13.8%	P; NR
HETM: N-(2-hydroxyethyl)-thiomorpholine	0.6-9.1%	A&P; NR
Other MEA substitution products	0.05-1%	A&P; NR
1,4-dithiane	0.008-0.16%	A; NR
RCRA TC Components[e] (above the regulatory limit):		
vinyl chloride	5.8-6.9 mg/L	T; D043[d]
Tetrachloroethylene	2.2-2.6 mg/L	T; D039[d]
Trichloroethylene	1.4-1.6 mg/L	T; D040[d]
selenium	3.0-3.6 mg/L	T; D010[d]
HD: bis-(2-chloroethyl) sulfide (chemical agent):		
HD	ND (< 50 ppb)	HD
Other Trace Components:		
1,1-dichloroethylene[f, g]	0.13-0.15 mg/L	T
chloroform[f, g]	0.14-0.2 mg/L	T
methyl ethyl ketone (MEK)[f, g]	0.33-0.37 mg/L	T
Trace Metals Found:		
arsenic[f, g]	140-230 ppb	T
chromium[f, g]	531-620 ppb	T
Copper	5.2-6.8 ppm	T; NR
Iron	2.3-3.0 ppm	T
Trace Metals Found (Continued):		
Manganese	ND-343 ppb	T
nickel[g]	130-1550 ppb	T
Vanadium	ND-720 ppb	T

HD Neutralent Composition[a,b]

NOTES:

a The major components of the neutralent composition are calculated based on analytical results and process knowledge. The TC and trace components listed are values obtained by analysis as described in Ac@ below. The analytical results were obtained from several methods as shown below.

b Abbreviations:
- ND: not detected by the means of analysis used.
- ppb: parts of component per billion parts of neutralent
- ppm: parts of component per million parts of neutralent
- TC: toxicity characteristic

c The following codes describe the source of the estimated composition:
- P: calculated from the stoichiometry and the path of the reaction
- A: estimated from the results of analyses of the HD neutralent
- T: the analytical results for RCRA toxicity characteristic components were obtained by EPA SW-846 Methods 8240B, 6010A, 8081, 8151; the metals were determined by an ICP/MS method of analysis for trace metals, developed by ERDEC for chemical agent neutralents and based on SW-846 Method 6020.
- HD: the results of ERDEC=s extraction and GC/MS method of analysis for HD in the neutralent after storage for 72 to 96 hours.
- NR: the component is not regulated as a TC substance by RCRA regulations.

d EPA Hazardous Waste Numbers applicable to HD neutralent waste stream because the concentration levels exceed the RCRA regulatory levels.

e During analysis, it was determined that the quantitation levels (limits of detection) were above the TC regulatory limits for six of the TC substances. Quantitation limits above the regulatory levels were for the following substances. (The waste code, the quantitation limit, and the regulatory limit, both in mg/L, are shown in parentheses.) : hexachlorobutadiene (D033, 2.0-5.0, 0.5); 2,4-dinitrotoluene (D030, 2.0-5.0, 0.13); hexachloroethane (D034, 3.3-5.0, 3.0); nitrobenzene (D036, 3.3-5.0, 2.0); 2,4,6-trichlorophenol (D042, 3.3-5.0, 2.0); and hexachlorobenzene (D032, 3.3-5.0, 0.13). Also, the neutralent samples could not be prepared for mercury (D009) analysis because of interference from the substances in the matrix.

f These materials are RCRA TC substances, but the levels found by analysis are below the regulatory limit.

g Potential underlying hazardous constituent.

Parameter	Test method	Result
ignitability, flash point < 140^{o}F	ASTM 93-90 (used Pensky Martens closed cup apparatus)	does not flash below 230^{o}F
Corrosivity	EPA 150.1	pH: 11.2-11.3[b]
Reactivity	SW-846, chapter 7.3.4, 903A; EPA 335.3	not unstable[c] and does not generate HCN at >250 mg/kg or H_2S at > 500 mg/kg

NOTES:

a These RCRA characteristics are based on the results of the EPA Tests and process knowledge.
Abbreviations:
- ASTM: American Society for Testing and Materials
- H_2S: hydrogen sulfide
- HCN: hydrogen cyanide
- EPA HWNo.: US Environmental Protection Agency=s RCRA Hazardous Waste Number from 40 CFR '261.24, Table 1 (1 July 1995).

b The corrosion of steel at 130^{o}F by the HD neutralent was not tested.

c The HD neutralent is not unstable, based on storage studies and known properties of the major components.

GB Neutralent Composition[a]

Major Components (Concentration: > 0.02%):	Calculated	Notes[c]:
water	49.4-49.9%	P; NR
MEA: monoethanolamine	33.9-40.3%	P; NR
MEA·IMP:2-hydroxyethylammonium O-isopropyl	0.7-8.5%	P&A;NR
MEA·HF: 2-hydroxyethylammonium fluoride or	0.4-4.6%	P; NR
GB-MEA: isopropyl 2-aminoethyl methylphosphonate	0.3-3.0%	A&P; NR
DIMP: diisopropyl methylphosphonate	0.03-0.36%	A&P; NR
TBA: tributylamine	0.2-0.017%	P; NR
DIPU: 1,3-diisopropylurea	45-530 ppm	P; NR
DIPTU: 1,3-diisopropylthiourea	17-200 ppm	P; NR
MEA·MPA 2-hydroxyethylammonium methylphosphonate	400-800 ppm	A; NR
other methylphosphonates	< 100 ppm	P; NR
RCRA TC Components[e] (above the regulatory limit):		
benzene	6.5-6.8 mg/L	T
GB, isopropyl methylphoshonofluoridate (chemical agent):		
GB	ND (< 25 ppb)	GB
Other Trace Components Found:		
methyl ethyl ketone (MEK)[f, g]	0.29-0.54 mg/L	T
Trace Metals Found:		
aluminum	76-81.5 ppm	T
arsenic[f, g]	660-760 ppb	T
barium[f]	ND-750 ppb	T
boron[h]	110-125 ppm[g]	T
chromium[f, g]	410-1080 ppb	T
iron	3.4-3.4 ppm	T
lead[f, g]	550-1300 ppb	T
manganese	1.8-2.2 ppm	T
Trace Metals Found (Continued):		
nickel[g]	410-500 ppb	T
vanadium	330-420 ppb	T

GB Neutralent Composition[a]

NOTES:

a The major components of the neutralent composition are calculated based on analytical results and process knowledge. The TC and trace components listed are values obtained by analysis as described in Ac@ below. The analytical results were obtained from several methods as shown below.

b Abbreviations:
- ND: not detected by the means of analysis used.
- ppb: parts of component per billion parts of neutralent
- ppm: parts of component per million parts of neutralent
- TC: toxicity characteristic

c The following codes are used to describe the source of the estimated composition:
- P: calculated from the stoichiometry and the path of the reaction
- A: estimated from the results of analyses of the GB neutralent
- T: the analytical results for RCRA toxicity characteristic components were obtained by EPA SW-846 Methods 8240B, 6010A, 8081, 8151; the metals were determined by an ICP/MS method of analysis for trace metals, developed by ERDEC for chemical agent neutralents and based on SW-846 Method 6020.
- GB: the results of ERDEC=s extraction and GC/MS method of analysis for GB in the neutralent after storage for 46 days.
- NR: the component is not regulated as a TC substance by RCRA regulations.

d Benzene concentration level exceeds the RCRA TC regulatory level.

e During analysis, it was determined that the quantitation levels (limits of detection) were above the regulatory limits for five of the TC substances. Quantitation limits above the regulatory levels were for the following substances. (The waste code, the quantitation limit, and the regulatory limit, both in mg/L, are shown in parentheses.): chlordane (D020, 0.06, 0.03), hexachlorobutadiene (D033, 1.0-1.6, 0.5); 2,4-dinitrotoluene (D030, 0.2, 0.13); hexachlorobenzene (D032, 0.2-1.6, 0.13); and toxaphene (D015, 0.8-2.0, 0.5).

f These materials are RCRA TC substances, however, the levels found by analysis were below the regulatory limit.

g Potential underlying hazardous constituent.

h The concentration of boron was found to be above the calibration level used in the method. Therefore, the results are considered estimates.

GB Neutralent[a]

Parameter	Test method	Result
ignitability, flash point < 140^{o}F	ASTM 93-90 (used Pensky Martens closed cup apparatus)	flash points: 170-188^{o}F
corrosivity	EPA 150.1	pH: 10.5-10.6[b]
reactivity	SW-846, 9030A; EPA 335.3 (see SW-846, chapter 7.3.4)	not unstable[c] and does not generate HCN at >100 mg/kg or H_2S at > 50 mg/kg

NOTES:

a These RCRA characteristics are based on analytical results and process knowledge. Abbreviations:
- ASTM: American Society for Testing and Materials
- H_2S: hydrogen sulfide
- HCN: hydrogen cyanide

b The corrosion of steel at 130^{o}F by the GB neutralent was not tested.

c The GB neutralent is not unstable, based on storage studies and known properties of the major components.

VX Neutralent Composition[a]

Major Components (Concentration: > 0.02%):	Calculated Result[a,b]	Notes[c]:
MEA: monoethanolamine	77.6-83.0%	P;NR
water	6.9-7%	P; NR
sodium hydroxide	4.2-6.3%	P;NR
NaTHIOL: sodium 2-diisopropylaminoethanethiolate	1.4-4.5%	A&P;NR
NaEMPA: sodium O-ethyl methylphosphonate	0.6-2.0%	A&P;NR
NaAEMPA: sodium O-(2-aminoethyl) methylphosphonate	0.5-1.8 %	A&P; NR
Na_2MPA: disodium methylphosphonate	0.15-0.5%	A&P; NR
ASULFIDE@: bis-(2-diisopropylaminoethyl) sulfide	0.22-0.71%	A&P; NR
ADISULFIDE@: bis-(2-diisopropylaminoethyl) disulfide	0.13-0.41%	A&P; NR
DIPAES: 2-diisopropylaminoethyl ethyl sulfide	0.03-0.09%	A&P; NR
1,3-dicyclohexylurea[d]	0.1-0.35%	P; NR
ethanol	0.2-0.7%	P; NR
other identified components[e]	ca. 0.4-1%	A&P; NR
VX: O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate:		
VX	ND (< 1 ppm)	VX
Trace Components (< 2 ppm)[f]:		
chromium[g, h]	380-400 ppb	T
lead[g, h]	1.2-1.4 ppm	T
vanadium	660-700 ppb	T

NOTES:

a The major components of the neutralent composition are calculated based on analytical results and process knowledge. The trace metals listed are values obtained by analysis as described in Ac@ below. The analytical results were obtained from several methods as shown below.

b Abbreviations:
ND: not detected by the means of analysis used.
ppb: parts of component per billion parts of neutralent
ppm: parts of component per million parts of neutralent
TC: toxicity characteristic

VX Neutralent Composition[a]

c The following codes are used to describe the source of the estimated composition:
P: calculated from the stoichiometry and the path of the reaction
A: estimated from the results of analyses of the VX neutralent
T: the metals were determined by an ICP/MS method of analysis for trace metals, developed by ERDEC for chemical agent neutralents and based on SW-846 Method 6020; the RCRA TCLP extraction and analyses for TC components have not yet been obtained on this laboratory-prepared VX neutralent.
VX: the results of ERDEC=s extraction and GC/MS method of analysis for VX in the neutralent after storage for 28-50 days.
NR: the component is not regulated as a TC substance by RCRA regulations.

d The 1,3-dicyclohexylurea is the product derived from the dicyclohexylcarbodiimide stabilizer that is present in munitions grade VX. Much of the VX that was made was stabilized with diisopropylcarbodiimide, and therefore, the derived neutralent from such VX will contain up to 0.3 percent of 1,3-diisopropylurea.

e The following components could be identified in the VX neutralent, but the quantities were not determined:
cyclohexylamine
2-diisopropylaminoethanol
ethylene glycol
N-(2-hydroxyethyl) methylphosphoramidate

The following components were also found, but they are assumed to form by reaction during extraction by methylene chloride used in the method of analysis:
2-(diisopropylamino)ethyl methyl sulfide (DIPAEMS or $RSCH_3$)*
chloromethyl 2-(diisopropylamino)ethyl sulfide (DIPAMS or $RSCH_2Cl$)*
N-2-[(chloromethylthio)methylthio]ethyl-N-isopropyl-2-propanamine ($RSCH_2SCH_2Cl$)*
N-2-[(2-diisopropylamino)ethylthiomethylthioethyl]-N-isopropyl-2-propanamine (VX Me disulfide or $RSCH_2SR$)*
* R = $(iPr)_2N\text{-}CH_2CH_2S$- ; iPr = $(CH_3)_2CH$- or isopropyl group

f As noted in footnote Ac,@ RCRA TC analyses were not performed on the laboratory-prepared VX neutralent.

g These materials are RCRA TC substances, however, the levels found by analysis were below the regulatory limit.

h Potential underlying hazardous constituent.

VX Neutralent Characteristics[a]

Parameter	Test method	Result
Ignitability, flash point < 140°F	No test performed	flash points should exceed 140°F
Corrosivity	No test performed	pH should exceed 14
Reactivity	No test performed	not unstable[b], but the neutralent may generate H_2S at > 250 mg/kg

NOTES:

a These RCRA characteristics are based on process knowledge. Abbreviations: H_2S: hydrogen sulfide
EPA HWNo.: US Environmental Protection Agency=s RCRA Hazardous Waste Number from 40 CFR '261.24, Table 1 (1 July 1995).

b The VX neutralent is not unstable, based on storage studies and known properties of the major components.

ATTACHMENT 4, APPENDIX A-2
MATERIAL SAFETY DATA SHEETS FOR CHEMICAL AGENTS AND INDUSTRIAL CHEMICALS